California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring
Environmental Hazards Assessment Program
1001 I Street
Sacramento, California 95814

2002 RICE PESTICIDES PROGRAM MONITORING PROTOCOL STUDY # 206

March 18, 2002

The 2002 Rice Pesticides Monitoring Program is a cooperative effort between the California Rice Commission and the Department of Pesticide Regulation (DPR). The standard operating procedures have changed from that of the 2001 program for the number of samples analyzed. In 2002 carbofuran, propanil, and triclopyr will not be monitored. Carbofuran is no longer used and concentrations of propanil and triclopyr in 2001 were below target levels of concern for human health effects or aquatic toxicity and DPR determined it was not necessary to monitor for propanil and triclopyr in 2002. Malathion and methyl parathion will be analyzed during the ten weeks toxicity tests are performed. The sampling schedule, estimated number of samples (tables 1 and 2), sample collection and delivery, and chain of custody procedures for Colusa Basin Drain (CBD5), Butte Slough (BS1), and the Sacramento River (SR1) are described in this protocol. Monitoring of CBD5, BS1, and SR1 will be conducted twice per week on Tuesdays and Thursdays throughout the pesticide application season.

The monitoring program will begin with background sampling in early April at all sample sites, two to three weeks prior to the first applications of rice pesticides, in the rice growing region of the Sacramento Valley. These samples will be collected by California Rice Commission consultant personnel in consultation with DPR staff.

There were no detections of lambda cyhalothrin at CBD5 in 2001. Therefore no monitoring was determined necessary in 2002.

Sampling Methods

Sampling for molinate, thiobencarb, methyl parathion, and malathion for the 2002 rice growing season will be performed by a consultant chosen by the California Rice Commission. As standard operating procedure, all sampling personnel will wear rubber gloves during sampling and if contamination is suspected, the gloves will be replaced.

Every attempt will be made to avoid both disturbing the bottom of the agricultural drain and sampling areas of the drain with no observable flow. All bottles and chain of custody records (COCs) will be provided by DPR. The consultant will be responsible for all bottle labeling and COC preparation. Samples will be collected using a Kemmerer water sampler (stainless steel and Teflon[7] model) at a depth equal to one-half the water column. The Kemmerer has a capacity of 1.5 liters, and a composite sample consisting of the appropriate volume of water to be split into the required number of samples are to be deposited in a stainless steel container. The volume of water to be collected is determined by the sampling schedule. The composite sample will then be homogenized and split into 1-liter amber bottles with Geotech® water splitter provided by DPR. A COC will accompany each sample bottle. Samples will then be stored on wet or blue ice (4^{o}C). All sampling equipment is to be cleaned immediately after sampling.

Samples to be analyzed for methyl parathion/malathion will be acidified with 3N HCl to a pH between 3.0 and 3.5 for increased sample stability during storage. All samples will be stored on wet or blue ice (4^{o}C) until delivered to the laboratory for analyses. Samples to be used for toxicity tests and backups will be collected as part of the primary volume of water. Backup samples will be collected and held in storage (4^{o}C) until the initial data analyses are complete.

Rinse blanks for each monitoring site will be prepared by pouring 4.5 liters of deionized water over the cleaned sampling equipment and collecting the resultant rinse water. The rinse water is then to be transferred to 1-liter amber bottles and submitted for analyses with the primary samples to the primary laboratories. This process will occur in weeks four and eight for a total of two samples per target chemical.

Water temperature, pH, and dissolved oxygen will be measured at each monitoring site during all sampling periods and the data recorded on the water quality sheet provided by DPR (Attachment 1).

Lab Analysis and Sample Delivery

The California Rice Commission consultant is responsible for sample delivery arrangements. Syngenta (registrant for Ordram®) will conduct primary analysis for molinate. Valent Dublin Laboratory will conduct primary analysis for thiobencarb. Primary sample analysis will be conducted by California Department of Food and Agriculture (CDFA) Laboratory for methyl parathion, malathion. CDFA Laboratory will also perform quality control analysis for molinate and thiobencarb. DFG laboratory will perform quality control analysis for methyl parathion and malathion pending contract finalization. Toxicity samples will be delivered by the California Rice Commission consultant to California Department of Fish and Game's Aquatic Toxicology Laboratory (ATL) in Elk Grove, California by the close of business (earlier if possible) on Tuesday of each week

Table 1. Sampling schedule for the 2002 Rice Pesticides Monitoring Program

DATE	Sampling Sites CBD5, BS1, SR1 All sites sampled twice weekly (Tuesdays and Thursdays for 2002 program*	
	Day 1	Day 2
Background (2 to 3 weeks prior to) beginning of pesticide application	III[c] + Tox[g] + QC	Not sampled
Week 1	I[a] + Tox[d]+WQ[f]	I[a] + QC[e] + WQ[f]
2	II[b] + Tox[d]+WQ[f]	II[b] + QC[e] + WQ[f]
3	II[b] + Tox[d]+WQ[f]	II[b] +QC[e] + WQ[f]
4	II[b] + Tox[d]+WQ[f] +RB[g]	II[b] + QC[e] + WQ[f]
5	II[b] + Tox[d]+WQ[f]	II[b] +QC[e] + WQ[f]
6	II[b] + Tox[d]+WQ[f]	II[b] + QC[e] + WQ[f]
7	II[b] +Tox[d]+WQ[f]	II[b] +QC[e] + WQ[f]
8	II[b] + Tox[d] +WQ[f]+RB[g]	II[b] + QC[e] + WQ[f]
9	II[b] +Tox[d]+WQ[f]	II[b] + QC[e] + WQ[f]
10	II[b] +Tox[d] +WQ[f]	II[b] + QC[e] + WQ[f]
11	III[c]+WQ[f]	III[c] + QC[e] + WQ[f]
12	III[c]+WQ[f]	III[c] + QC[e] + WQ[f]

a) Group I: methyl parathion and malathion.
b) Group II: methyl parathion, malathion, thiobencarb, molinate
c) Group III: thiobencarb, molinate
d) Tox: Toxicity testing
e) QC: Quality Control*
f) WQ: Water Quality parameters measured
g) RB: Rinse Blank

***Quality control samples are collected on Thursdays at all monitoring sites.**

Table 2. Estimated number of primary and quality control samples from CBD5, BS1, and SR1 for the routine 2002 Rice Pesticides Monitoring Program.

Background Samples

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) mp/mn (DFG)	(P) mp/mn (DFG)	(P) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(P) me/tb (CDFA)	(P) me/tb (CDFA)	(P) me/tb (CDFA)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 1

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 2

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 3

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 4- Rinse blanks at all sites to be delivered to the primary laboratories.

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta
(RB) mp/mn (CDFA)	(RB) mp/mn (CDFA)	(RB) mp/mn (CDFA)
(RB) thiobencarb (Valent)	(RB) thiobencarb (Valent)	(RB) thiobencarb (Valent)
(RB) molinate (Syngenta)	(RB) molinate (Syngenta)	(RB) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 5

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 6

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 7

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 8- Rinse blanks at all sites to be delivered to the primary laboratories.

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(RB) mp/mn (CDFA)	(RB) mp/mn (CDFA)	(RB) mp/mn (CDFA)
(RB) thiobencarb (Valent)	(RB) thiobencarb (Valent)	(RB) thiobencarb (Valent)
(RB) molinate (Syngenta)	(RB) molinate (Syngenta)	(RB) molinate (Syngenta)
water quality	water quality	water quality
(T) toxicity (ATL)		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 9

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality

Week 10-Final week of aquatic toxicity tests

Tuesday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(T) toxicity (ATL)	water quality	water quality
water quality		
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) mp/mn (CDFA)	(P) mp/mn (CDFA)	(P) mp/mn (CDFA)
(QC) mp/mn (DFG)	(QC) mp/mn (DFG)	(QC) mp/mn (DFG)
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 11

Tuesday

CBD5	BS1	SR1
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Week 12

Tuesday

CBD5	BS1	SR1
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

Thursday

CBD5	BS1	SR1
(P) thiobencarb (Valent)	(P) thiobencarb (Valent)	(P) thiobencarb (Valent)
(P) molinate (Syngenta)	(P) molinate (Syngenta)	(P) molinate (Syngenta)
(QC) me/tb (CDFA)	(QC) me/tb (CDFA)	(QC) me/tb (CDFA)
water quality	water quality	water quality
BA1-acidified back-up	BA1-acidified back-up	BA1-acidified back-up
BU1-unacidified back-up	BU1-unacidified back-up	BU1-unacidified back-up

a) Molinate and thiobencarb are analyzed in a single sample by the primary and quality control laboratories.
b) Methyl parathion and malathion are analyzed in a single sample by the quality control laboratory.

KEY TO ABBREVIATIONS:

P	Primary (sample)	me/tb	molinate/thiobencarb
QC	Quality Control (sample)	mp/mn	methyl parathion/malathion
RB	Rinse Blank (sample)		
BA	Back-up (acidified)		
BU	Back-up (unacidified)		

Total Chemical Analyses	(Routine Rice Pesticides Program monitoring: samples for primary analyses)=207 samples (Samples for quality control (63) + 18 rinse blanks) =81 samples
Toxicity	(1 sample/wk x 10 wks + background)=11samples

Sample Total=299 samples

Attachment 1

WATER QUALITY SHEET

STUDY NUMBER 206
2002 RICE PESTICIDES PROGRAM

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
DEPARTMENT OF PESTICIDE REGULATION
ENVIRONMENTAL MONITORING
ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM
1001 N STREET
SACRAMENTO, CALIFORNIA 95814-5624

DATE/TIME: _____ CREW: _____

LOCATION: _____

WATER TEMPERATURE (EC): _____ AIR TEMPERATURE:_____

DISSOLVED OXYGEN (mg/L): _____ CALIBRATED AT:_____

WATER pH: _____ (NUMBER OF DROPS OF 3 N HCl _____ TO A pH OF_____
IN THE CONSULTANT LABORATORY)

COMMENTS:

WATER DEPTH: _____ VOLUME OF WATER COLLECTED: